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(54) METAL WORKING FLUIDS FOAM CONTROL AGENT

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(56) References Cited

U.S. PATENT DOCUMENTS

4,339,342 A		Hempel et al.
5,360,560 A		Schmid et al.
7,348,460 B2		Wulff et al.
9,381,450 B2		~
011/028/993 A1	* 11/2011	Shibata C10M 105/12
		508/583

FOREIGN PATENT DOCUMENTS

CN	106479654	3/2017	
CN	107034003	8/2017	
CN	107502910	12/2017	
CN	111013201 A	4/2020	
EP	0484542 A1	* 11/1995	C10M 101/02
JP	2005330236	* 12/2005	

OTHER PUBLICATIONS

PCT/CN2020/123535 International Search Report and Written Opinion with a mailing date of Jul. 29, 2021.

Office Action from corresponding Taiwan Application: 110135170 with a mailing date of Apr. 24, 2023.

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(57) ABSTRACT

A foam control agent and method of controlling foam for metal working fluids by use of a foam control agent, wherein the agent comprises at least a branched alcohol.

3 Claims, No Drawings

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METAL WORKING FLUIDS FOAM **CONTROL AGENT**

Embodiments relate to a foam control agent and method of controlling foam for metal working fluids, wherein the 5 agent comprises at least a branched alcohol.

INTRODUCTION

Metal working fluids (MWFs) are used for lubrication of 10 metal cutting and tool forming. These fluids provide cooling for the metal work tooling, removal of cutting chips from the tool/work piece interface and help provide an acceptable soluble oil, semi-synthetic fluid or synthetic fluid. Neat oil and soluble oil contain 50-70 wt. % oil and oil-soluble anti-wear/extreme pressure additives. They provide excellent lubricity but poor cooling efficiency. A synthetic metal working fluid is mainly composed of water with lubricant 20 additives. It provides excellent properties for removing the heat generated during the processing but only average lubricity.

A semi-synthetic fluid differs from soluble oil and synthetic metal working fluids, in that it contains a significant 25 amount of water, but also 10-30 wt. % mineral oil, 10-30 wt. % emulsifiers and other functional additives. Fatty acid ethanolamine soaps, sodium alkane sulfonates, alcohol ethoxylates and other surfactants are used to disperse mineral oil or plant oil into the water and thus provide proper ³⁰ lubricity to the tool metal contacting a work surface. These surface-active agents contribute to the generation of large amounts of foam during the metal working process, which causes insufficient liquid lubricity between the tool and the working piece. In some cases, this lack of lubricity can cause ³⁵ liquid overflow from the fluid bath. Some machining processes (especially grinding) are very sensitive to foam and require particular care when planning the processing.

Silicone based foam control agents are widely used in MWFs to address the foaming issue due to these agents very low surface tension and insolubilities in both oil and water. However, the biodegradability of silicone defoamers is not good, and they also lack stability in many MWF formulations. Additionally, the deposition of silicone onto the surface of the metal impacts the (smooth) finishing which also 45 creates additional issues for any subsequent painting step(s).

For all these reasons and more, there is a need for a foam control agent and method of controlling foam for metal working fluids.

SUMMARY

Embodiments relate to a foam control agent and method of controlling foam for metal working fluids, wherein the agent comprises at least a branched alcohol.

DETAILED DESCRIPTION

The present disclosure relates to a foam control agent for metal working fluids (MWFs). The present disclosure details 60 how, unexpectedly, branched alcohols have been shown to have superior foam control performance. The branched alcohols may be 2-alkyl-1-alkanols (also known as Guerbet alcohols), and preferably 2-ethylhexanol (2-EH) and 2-propylheptanol (2-PH). The Guerbet alcohols including 65 2-butyl-1-octanol. These alcohols can be synthesized via the aldol condensation of the corresponding aldehydes or from

the Guerbet reaction of primary linear alcohols. Other methods of production may also be utilized.

The generic structure of the antifoaming agent currently disclosed is as follows:

$$R$$
 $H_{3}C$
 OH

wherein x is an integer from 2 to 14 and R is an alkyl group with 1-14 carbon atoms.

The foam control agent may also be described as compost-machining finished surface. MWFs may be neat oil, 15 prising a 2-alkyl substituted alcohol from C8-C32. The alcohols can be predominately one isomer (>95 wt. %) or a mixture of alcohols which can be generated by an aldol condensation of a mixture of aldehydes or generated from a mixture of alcohols via the Guerbet reaction.

> The C8-C32 Guerbet alcohols including 2-ethylhexanol and 2-propylheptanol and the mixture of C8, C9, and C10 alcohols generated from the aldol condensation of butyraldehyde and valeraldehyde are preferred in some embodiments.

> The concentration of the Guerbet alcohol in the formulated foam control agent ranges from 0.01% to 100%, preferably, ranging from 30% to 100%. The Guerbet alcohol can be in the form of a solid or liquid, a liquid is preferred. If it is a solid, the material may be dissolved or dispersed in a solvent. The said foam control agent can be aqueous solution or organic solvent based solution. The usage dosage of the said foam control agent for MWFs may vary. The usage dosage of this foam control agent for MWFs ranges from 0.01% to 5%, preferably, ranges from 0.1% to 1%.

> Other foam control agents (e.g., copolymers composed of ethylene oxide, propylene oxide, and/or butylene oxide, random or blocks) or other hydrophobic materials such as waxes, oils or silicas may also be added with the branched, Guerbet alcohol(s). Silicon defoamers can be used in conjunction with the 2-alkyl alcohols. Surfactants, especially alkoxylates of the alcohols can also be used. The use of branched alcohols as foam control agents may be water based or oil based.

> The new foam control agent presently disclosed may be in the form of a solid or liquid. If it is a solid, the material may be dissolved or dispersed in a solvent before use as a foam control agent. The presently disclosed agents are believed to work in the presence of all commonly used metal working fluids.

The chemical agent can be used both in antifoamer or defoamer formulations. Antifoamer formulations are obtained by the mixture of polyglycols, esters, silicones, solvents, water and/or other chemicals that in the gas-liquid interface of the bubble avoiding the foam formation. Other 55 amphiphilic chemicals based on block copolymer can be used as well. In defoaming formulations, in addition to the products mentioned above, it can be used vegetable oils, mineral oils, waxes and other oily agents.

The optional surfactant or emulsifier contained in the foam control agent is selected to be suitable for improving the compatibility of the foam control agent on the feedstock or forming an emulsion with the composition of branched alcohol. The optional surfactant or emulsifier has an amount ranging from 0.1-30% by weight of the composition of branched alcohol.

The optional surfactant or emulsifier may be anionic, cationic or nonioic. Examples of suitable anionic surfactants 3

or emulsifiers are alkali metal, ammonium and amine soaps; the fatty acid part of such soaps contains preferably at least 10 carbon atoms. The soaps can also be formed "in situ;" in other words, a fatty acid can be added to the oil phase and an alkaline material to the aqueous phase.

Other examples of suitable anionic surfactants or emulsifiers are alkali metal salts of alkyl-aryl sulfonic acids, sodium dialkyl sulfosuccinate, sulfated or sulfonated oils, e.g., sulfated castor oil; sulfonated tallow, and alkali salts of short chain petroleum sulfonic acids.

Suitable cationic surfactants or emulsifiers are salts of long chain primary, secondary or tertiary amines, such as oleylamide acetate, cetylamine acetate, di-dodecylamine lactate, the acetate of aminoethyl-aminoethyl stearamide, dilauroyl triethylene tetramine diacetate, 1-aminoethyl-2- 15 heptadecenyl imidazoline acetate; and quaternary salts, such as cetylpyridinium bromide, hexadecyl ethyl morpholinium chloride, and diethyl di-dodecyl ammonium chloride.

Examples of suitable nonionic surfactants or emulsifiers are condensation products of higher fatty alcohols with 20 ethylene oxide, such as the reaction product of oleyl alcohol with 10 ethylene oxide units; condensation products of alkylphenols with ethylene oxide, such as the reaction product of isoctylphenol with 12 ethylene oxide units; condensation products of higher fatty acid amides with 5, or 25 more, ethylene oxide units; polyethylene glycol esters of long chain fatty acids, such as tetraethylene glycol monopalmitate, hexaethyleneglycol monolaurate, nonaethyleneglycol monostearate, nonaethyleneglycol dioleate, tridecaethyleneglycol monoarachidate, tricosaethyleneglycol 30 monobehenate, tricosaethyleneglycol dibehenate, polyhydric alcohol partial higher fatty acid esters such as sorbitan tristearate, ethylene oxide condensation products of polyhydric alcohol partial higher fatty acid esters, and their inner

4

anhydrides (mannitol-anhydride, called Mannitan, and sorbitol-anhydride, called Sorbitan), such as glycerol monopalmitate reacted with 10 molecules of ethylene oxide, pentaerythritol monooleate reacted with 12 molecules of ethylene oxide, sorbitan monostearate reacted with 10-15 molecules of ethylene oxide, mannitan monopalmitate reacted with 10-15 molecules of ethylene oxide; long chain polyglycols in which one hydroxyl group is esterified with a higher fatty acid and other hydroxyl group is etherified with a low molecular alcohol, such as methoxypolyethylene glycol 550 monostearate (550 meaning the average molecular weight of the polyglycol ether). A combination of two or more of these surfactants may be used; e.g., a cationic may be blended with a nonionic or an anionic with a nonionic.

The foam control agent may further comprise one or more additives. Examples of additives include ethylene oxide/propylene oxide block copolymers, butylene oxide/propylene oxide block copolymers, ethylene oxide/butylene oxide block copolymers, waxes, or silicone-based materials. For other cleaning applications where surfactants cause foaming in cleaning steps Higher 2-alkyl substituted alcohols up to C32 can be used.

The foam control agent herein described can be used in semi-synthetic MWF or synthetic MWF comprising a Tall oil acid, ethanolamine, KOH, polyalkyl glycol lubricant, alcohol ethoxylates, sodium alkane sulfonate and water. The foam control agents described herein also help maintain transparency of a given MWF and are also biodegradable.

Examples

An experiment to test the efficacy of the presently disclosed foam control agent and others may be conducted as follows.

TABLE 1

		TABLE 1				
Raw Materials Used for Experiments						
Name	Producer/Vendor	Purpose	Chemistry and function			
2-butyl-1-octanol (2-BO)	Sigma Aldrich	Tested example	HO			
2-ethylhexanol (2-EH)	Sigma Aldrich	Tested example	OH			
2-Propylheptanol (2-PH)	Sigma Aldrich	Tested example	OH			
AFE-1510 ANTA L-61	Dow Corning Sasol	Comparative example Comparative example	Silicone based foam control agent EO/PO copolymer			
FoamBan 3057	Munzing Shanghai Co., Ltd	Comparative example	Petroleum distillates, solvent dewaxed light paraffinic and Petroleum distillates, solvent dewaxed heavy paraffinic			
Isobutanol	The Dow Chemical	Comparative example	Isobutanol			
C12-C14 linear alcohol	Sasol	Comparative example	C12-C14 linear alcohol			
Exxal 13	Exxonmobil	Comparative example	Iso-C13 Alcohol			
SY-2	Local MWF	Commercial MWF	Synthetic MWF, Toll oil			
	formulator	product without	acid + ethanolamine + KOH + water + poly alkyl			
		foam control agent	glycol lubricant			

TABLE 1-continued

Raw Materials Used for Experiments					
Name	Producer/Vendor	Purpose	Chemistry and function		
SY-6	Local MWF formulator	Commercial MWF product without foam control agent	Semi-synthetic MWF, 40% mineral oil + tall oil acid + ethanolamine + Alcohol Ethoxylates + Sodium Alkane Sulfonate		
BLC	AFTON	Commercial MWF product without foam control agent	Semi-synthetic MWF, 20-30% mineral oil + 10-19.9% tall oil, monoethanolamine salt + 10-19.9% long-Chain alkyl alkanol amide + 1-5% Hexylene glycol + 1-5.0% ethanol, 2- amine + water to 100%		

Test 1—Antifoaming Shake Test

A screening shake test was first conducted to evaluate the presently disclosed foam control agents and some comparative examples. The concentrated commercial metal working fluid BLC was diluted 20 times using DI water. The tested defoamer was then added at 0.05% (500 ppm) to prepare 2 grams of solution in an 8 ml vial. The vial was then shaken for 1 hour in a lab shaker at a high-speed setting and the results of this test were recorded in Table 2 below.

TABLE 2

Vial Shaking Screening Results						
Example No.	MWF type	Foam Control Agent	Foaming appearance			
Comparative Example 1	BLC	No	Significant Foam			
Comparative Example 2	BLC	AFE-1510	Little Foam			
Example 1	BLC	2-PH	Little Foam			
Example 2	BLC	2-EH	Little Foam			
Example 3	BLC	2-BO	Little Foam			

15 Test 2—Defoaming Shake Test

The tested examples and comparative examples were then further evaluated by mixing them with other common commercial MWF formulations. Samples shown in Table 3 were prepared by dissolving 0.100 g foam control agent into 9.900 g semi-synthetic/synthetic MWF and shaking the mixture to give a homogeneous solution. A specially designed cylinder was used to evaluate the extent of foaming. The distance between the 0 mL mark and the 250 mL mark of the cylinder is 20-21.5 cm, and the distance between the 250 mL mark and the bottom of the stopper is approximately 4 to 6 cm. 2.50 g soluble oil or semi-synthetic MWF concentrate was then added into the 250 mL cylinder containing 95 mL of a standard 25 ppm hard water. After closing the cylinder with a stopper, the cylinder was inverted 30 times within 1 minute and the initial foam at time 0 seconds, as well as the foam level at 30 seconds, at 1 min, at 2 min and at 3 min was recorded.

The standard hard water (25 ppm) utilized for this test was prepared by adding anhydrous calcium chloride (0.045 g) and magnesium chloride hexahydrate (0.023 g) in DI water to prepare 2.0 L of standard hard water at 25 ppm.

TABLE 3

Standard Cylinder Inversion Results								
Example	MWF		Appearance				g, mL	
No.	type	Defoamer	after 24 h	Initial	30 s	60 s	120 s	180 s
Comparative example 1	SY-2	N/A	Transparent	175	175	170	170	170
Example 2	SY-2	2-PH	Transparent	130	95	10	0	0
Example 3	SY-2	2-BO	Transparent	125	110	72	20	5
Example 4	SY-2	2-EH	Transparent	160	140	105	45	5
Comparative example 5	SY-2	ANTA L-61	Transparent	145	140	100	25	20
Comparative example 6	SY-2	FoamBan 3057	Hazy	130	95	35	5	5
Comparative example 7	SY-2	Isobutanol	Transparent	150	150	140	75	50
Comparative example 8	SY-2	C12-C14 linear alcohol	Transparent	170	170	100	25	23
Comparative example 9	SY-2	Exxal 13	Hazy	140	135	110	25	20
Comparative example 10	SY-6	N/A	Transparent	170	170	170	170	170
Example 11	SY-6	2-BO	Transparent	135	125	115	110	110
Comparative Example 12	SY-6	ANTA L-61	Transparent	180	180	170	170	170
Comparative Example 13	SY-6	FoamBan 3057	Hazy	160	155	150	14 0	140
Comparative Example 14	SY-6	Isobutanol	Transparent	145	140	135	130	130
Comparative Example 15	SY-6	C ₁₂ -C ₁₄ linear alcohol	Hazy	135	135	130	130	130
Comparative Example 16	SY-6	Exxal 13	Hazy	145	140	140	140	140

As shown in Table 3, in a typical synthetic MWF formulation, 1% dosage of the three tested branched alcohols helped increase the foaming collapse compared to the blank sample. 2-PH displayed the best defoaming performance and was stable in the formulation compared to the existing 5 non-silicone defoamer in the market. In a typical semisynthetic MWF containing higher content high foaming emulsifiers, 2-BO presented better defoaming property compared to recognized foam control agent FoamBan 3057 and 2-BO was also more stable in the formulation and main- 10 tained transparency.

The invention claimed is:

- 1. A method of controlling foam for metal working fluids comprising the step of adding a foam control agent to the metal working fluid, wherein the agent comprises 2-butyl- 15 1-octanol, or 2-propylheptanol.
- 2. The method of claim 1, wherein at least one other foam control agent or hydrophobic material is used.
- 3. The method of claim 1, wherein the metal working fluid, when combined with the foam control agent, is trans- 20 parent.

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